MAGNETITE IN ALH 84001: PRODUCT OF THE DECOMPOSITION OF FERROAN CARBONATE. Adrian J. Brearley, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA; e-mail; brearley@unm.edu

Introduction: One of the major arguments presented by McKay et al. [1] as evidence for possible fossil life in ALH 84001 is the presence of fine-grained magnetite associated with carbonates. The morphologies and grain sizes of the magnetites were argued to be typical of magnetites produced by bacterial activity on Earth, suggesting that they are of biogenic origin. This hypothesis has, however, been challenged by Bradley et al. [2] who did not observe magnetites with cuboid, teardrop and irregular morphologies. Instead, [2] reported whiskers and platelets of magnetite with axial screw dislocations which were interpreted as vapor phase condensates formed from a cooling high temperature vapor. Such an origin clearly precludes low temperature formation for the host carbonates. However, because of the morphological differences between the magnetites observed by [1] and [2], there is a question as to whether the results of [2] satisfactorily explain the origin of both sets of magnetites.

In order to address this question further I have examined carbonates from specific petrologic occurrences in ALH 84001. My observations provide new evidence that an alternative hypothesis provides a more coherent explanation for the presence of magnetite in Fe-carbonates in ALH 84001. Rather than being of primary origin, these observations strongly suggest that the magnetites formed by decomposition of the siderite component of the carbonate following shock (re)melting of plagioclase-rich glass.

Carbonate in ALH 84001 is commonly associated with feldspathic glass [3,4,5] which formed by shock. ALH 84001 appears to have experienced at least two shock events, one which preceded carbonate formation and a second, later event which disrupted the carbonate globule stratigraphy [4]. Although the glass may have formed during the first shock event [5], new data demonstrate that the second shock event was of sufficient magnitude to (re)melt and mobilize the feldspathic glass. This is demonstrated by the presence of fragments of carbonate globules isolated within the carbonate melt [6]. These textures can only have formed as a result of the invasion and disruption of the carbonate globules by a melt phase. There is also evidence to suggest that some carbonate was actually replaced or dissolved within the feldspathic melts [7].

Results: In this study we have used SEM and TEM techniques to examine fragments of carbonate, 10-30 μm in size, which occur embedded in feldspathic glass within fracture zones in ALH 84001. The microstructures of these carbonates are extremely instructive in elucidating the origin of the magnetite in ALH 84001. On the TEM scale the fragments have planar interfaces with the glass and these surfaces are almost invariably the carbonate cleavage surfaces. The carbonate has a complex mottled contrast, indicative of strain in the lattice. One of the dominant features of the carbonate is the presence of myriad, randomly oriented magnetite inclusions. They have grain sizes from <10 nm up to 100 nm and have cuboid, teardrop and irregular, subrounded morphologies. Rare elongate grains also occur. High resolution TEM studies show that the magnetites are completely defect free. All these characteristics are identical to those described by [1] and confirm their observations. The carbonate is also characterized by a porous appearance and contains many voids which are often associated with individual magnetite grains. However, small voids also occur throughout the carbonate which are usually subrounded, but may also be partially faceted, with a shape close to that of carbonate rhombs. The size of the voids varies from <10 nm up to 50 nm. One potential concern is that the voids are the result of beam damage of the carbonate in the electron beam. However, this seems improbable since a) the voids do not change in shape or abundance as a function of time and b) siderite and ankerite are both quite stable under the electron beam [8,9] Analytical electron microscopy of the carbonate associated with the magnetite has a composition $Cc_{22}Mg_{44}Sd_{34}$, i.e. is ankeritic.

Discussion: In their TEM study of a carbonate globule in ALH 84001, McKay et al [1] observed magnetite in two distinct zones of very Fe-rich carbonate, one located in a thin band at the rim of the globule and a second located more towards the interior of the carbonate. Although the compositions of these Fe-rich carbonate bands were not reported, they probably have a composition close to $Cc_{12}Mg_{44}Sd_{44}$, based on compositional profiles across a similar carbonate globule in ALH 84001 [10]. The composition of these growth zones is consequently about 10 mol% richer in siderite than the next most Fe-rich carbonate composition in ALH 84001 [3,4]. McKay et al. [1] did not report any significant concentrations of magnetite in more Mg-rich carbonate growth bands. However, [2] reported that magnetites with platelet and whisker morphologies were distributed throughout the carbonate globules, but provided no data on the compositional range of the associated carbonate.

Several new observations in this study lead to a very different hypothesis for the origin of the fine-grained magnetite than that proposed by [1]. These observations are (1) the feldspathic glass was (re)melted after carbonate formation and disrupted the carbonates, (2) small fragments of carbonate, surrounded by glass, contain magnetites with identical

ORIGIN OF MAGNETITE IN ALH 84001: A.J. Brearley

grain sizes, morphologies and crystal perfection to those observed by [1], (3) the abundance of magnetite in this carbonate is lower than that observed by [1], (4) the composition of the carbonates associated with these magnetites is at least 10 mol% poorer in siderite than that associated with the magnetite described by [1], (5), the carbonate fragments that contain magnetite are highly porous in character and contain numerous voids, many of which are associated with individual magnetite particles. We interpret these observations as follows: the fragmentation of carbonate must have occurred when the feldspathic impact melt was hot and molten. As a consequence any carbonate fragments can be considered to be xenolithic material and must have been heated to some degree during this process. Estimates of postshock temperatures for feldspathic melts are on the order of 900°C [12], enough to affect the carbonates even if the heating event was short-lived. During this heating, partial decomposition of the carbonate occurred resulting in decarbonation and the formation of voids. There are no data on the thermal decomposition of carbonate with a composition such as that found in ALH 84001. However, it is well known that siderite has a much lower thermal stability than magnesite or calcite, so that the siderite component in solid solution would decompose preferentially and at a lower temperature. Even at temperatures as low as 385°C, siderite decomposition can be detected by weight loss [12] and Mössbauer spectroscopy [13]. In a vacuum, FeO is the dominant reaction product, but even at very low pO_2, magnetite is produced [13]. In contrast, magnesite appears to be stable to temperatures of at least 650°C [14] and calcite ~985°C. These results are also consistent with phase relations determined for carbonates in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ in metamorphic rocks [15]. Siderite is only stable at temperatures <550°C.

This model also provides a consistent explanation for the following features of magnetite and carbonate in ALH 84001. The concentration of magnetite in Fe-rich carbonate bands [1] is produced because this carbonate composition is the least thermally stable and will produce the most magnetite on decomposition. The voids in the carbonate are produced by the loss of CO_2 resulting from the decomposition of the siderite component in solid solution. The very fine-grained character of the magnetite is the result of rapid thermal decomposition caused by the heating associated with the shock melting of the feldspathic glass. In this type of disequilibrium process, where the stability limit of a phase is overstepped by a large temperature interval, nucleation at many different sites occurs very rapidly, because the activation energy for nucleation is exceeded for essentially all nucleation sites. The heating event was too short-lived to allow any reequilibration of the complex zoning observed in the carbonate. The low abundance of magnetite within most carbonate globules probably results from a thermal gradient across the globules, such that less Fe-rich carbonate compositions are not heated to sufficiently high temperatures to induce decarbonation. In comparison, small carbonate fragments with much lower Fe contents, isolated in the glass, were heated to higher temperatures, because they were completely surrounded by shock melt.

Finally, this model can also be used to explain the oxygen isotopic compositional variations between Fe-rich and Mg-rich carbonates in ALH 84001 [16]. Valley et al. [16] found that Mg-rich carbonates have $\delta^{18}O$‰ values between 18-22‰ whereas $\delta^{18}O$ for Fe-rich carbonates is much more variable and lower (8-18‰). The effect of decarbonation is to decrease the $\delta^{18}O$ value of the carbonate [17]. This could explain the lower $\delta^{18}O$ for Fe-rich carbonates assuming both Mg- and Fe carbonates had similar oxygen isotopic compositions before shock heating. The higher variability of $\delta^{18}O$ in the Fe-carbonate can be attributed to different degrees of decarbonation, depending on how much an individual carbonate grain was heated. In comparison, Mg-rich carbonates were more stable and largely unaffected by the heating event.

Conclusions: The fine-grained magnetites observed in carbonates in ALH 84001 did not form by biogenic processes, but by the thermal decomposition of Fe-bearing carbonate. This decarbonation reaction resulted from the shock heating and melting of feldspathic glass which is found in intimate association with carbonate. This conclusion puts the proposed hypothesis for fossil life on Mars into severe doubt.

References: [1] McKay, D.S. et al. (1996) Science 273, 924-929. [2] Bradley et al. (1996) GCA 60, 5149-5155. [3] Mittlefehldt, D.W. (1994) Meteoritics 29, 214-221. [4] Treiman, A.H. (1995) Meteoritics 30, 294-302.[5] Gleason, J.D. et al. (1997) GCA 61, 3503-3512. [6] Shearer, C.S. and Adcock, C. (1998) This vol.[7] Brearley, A.J. (1998) This vol. [8] Barber, D.J. and Riaz Khan, M. (1987) Min. Mag. 51, 71-86. [9] Wenk, H.-R. et al. (1991) Phys. Chem. Min. 17, 527-539. [10] Shearer, C.S. et al. (1997) LPSC XXVIII, 1295-1296.[11] Stöffler, D. et al. (1988) In Meteorites and the Early Solar System, pp.165-202. [12] Gallagher, P.K. et al. (1981) Thermochim. Acta 50, 41-47. [13] Gallagher, P.K. and Warne, S. St J. (1981) Thermochim. Acta 50, 253-267. [14] Harker, R.I. and Tuttle, O.F. (1955) Am. J. Sci. 253, 209-224. [15] Essene, E.J. (1983) Reviews in Mineralogy, Vol 11, 77. [16] Valley, J.W. et al. (1997) Science 275, 1633-1638. [17] Valley J.W. (1996) RIMS Vol 16, 445.
Acknowledgements: This research was supported by NASA grant NAG5-4935 to A.J. Brearley, P.I.